Asian Journal of Chemistry Vol. 7, No. 1 (1995), 109–117

Selenium(IV) Derivatives of N-(*o*-Hydroxy Substituted Benzyl) Alanines

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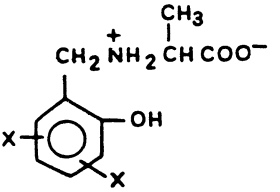
Several selenium(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines have been prepared by the interaction of selenium tetraisopropoxide with the latter in 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 2 : 3 molar ratios in benzene medium The various compounds thus prepared were obtained generally as coloured solids. However, amongst them those containing isopropoxy group(s) were found to be hygroscopic. All these compounds were characterized by azeotrope and elemental analysis, as well as by IR and PMR spectral measurements.

INTRODUCTION

Preparation of several metallo(IV) (silicon and titanium) derivatives of N-(*o*-hydroxy substituted benzyl) alanines *via* the reactivity of the corresponding metallo(IV) tetraisopropoxide and their characterization by suitable physico-chemical methods have been reported earlier.[1,2] The work described here deals with the preparation of selenium(IV) derivatives of N-(*o*-hydroxy substituted benzyl) alanines(I), *viz.*, (i) N-(2-hydroxy-3-methyl benzyl) alanine (H_3hmba-3), (ii) N-(2-hydroxy-6-methyl benzyl) alanine (H_3hmba-6) and (iii) N-(2-hydroxy-5-methyl benzyl) alanine (H_3hmba-5).



Where X = −H or −CH_3

(I)

EXPERIMENTAL

Owing to highly hygroscopic nature of selenium tetraisopropoxide stringent precautions were taken to exclude moisture throughout the experiments, as before[1,2].

Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures reported earlier[1,2]. Selenium

tetraisopropoxide was prepared by sodium method[3]. The various N-(*o*-hydroxy substituted benzyl) alanines were prepared by the method reported before[4]. Selenium was estimated in its elementary form by digesting the analytical sample with fuming nitric acid followed by passage of SO_2 in the presence of HCl which resulted in the precipitation of selenium quantitatively[5,6]. The instrumental details are reported earlier.

Reaction between Selenium Tetraisopropoxide and H_3hmba-3; 1:1 Molar Ratio

A mixture of $Se(OPr^i)_4$ (0.6850 g; 2.1737 mmol) and H_3hmba-3 (0.4500g; 2.1684 mmol) suspended in dry benzene (60 mL) taken in a R.B. flask was refluxed on a wax bath (90–95°C), using a fractionating column (30 cm long). After *ca.* 12 h of reflux isopropanol liberated during the course of reaction was removed azeotropically and determined by an oxidimetric method[1]. On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, $Se(OPr^i)$ (hmba-3) isolated as a brown coloured solid which was washed with benzene (3–4 times) followed by dry ether (2–3 times), and then dried under suction. The product was found to be soluble in DMF, DMSO and ethanol but insoluble in other common organic solvents like benzene, toluene, ether, chloroform and carbon tetrachloride. The compound was further purified by recrystallization from dry ethanol.

It may be mentioned here that since $Se(OPr^i)_4$ is soluble in benzene, while H_3hmba-3 is insoluble, the latter was taken in slightly less than the required stoichiometric amount in order to avoid contamination of impurities likely to occur by unreacted H_3hmba-3. The amount of isopropanol liberated was, therefore, calculated according to the amount of I taken in each case.

The relevant analytical details, characteristic IR frequencies and PMR data are summarized in Tables 1–3, respectively.

RESULTS AND DISCUSSION

It may be recalled here that N-(*o*-hydroxy substituted benzyl) alanines exist in zwitterionic form [Structure (I)][1]. The various reactions between selenium tetraisopropoxide and H_3hmba-3 may be illustrated as:

$$Se(OPr^i)_4 + H_3\text{hmba-3} \longrightarrow Se(OPr^i)(\text{hmba–3}) + 3Pr^iOH \quad (1)$$

$$Se(OPr^i)_4 + 2H_3\text{hmba-3} \longrightarrow Se(\text{Hhmba–3})_2 + 4Pr^iOH \quad (2)$$

$$Se(OPr^i)_4 + 3H_3\text{hmba-3} \longrightarrow Se(OPr^i)(H_2\text{hmba–3})_3 + 3Pr^iOH \quad (3)$$

$$Se(OPr^i)_4 + 4H_3\text{hmba-3} \longrightarrow Se(H_2\text{hmba–3})_4 + 4Pr^iOH \quad (4)$$

$$2Se(OPr^i)_4 + 3H_3\text{hmba-3} \longrightarrow [Se(OPr^i)]_2(\text{Hhmba–3})_3 + 6Pr^iOH \quad (5)$$

Identical reactions followed in case of H_3hmba-6 and H_3hmba-5 (yield (%): 92–95.

The IR spectrum of $Se(OPr^i)$(hmba-3) shows a medium broad band in the region 3150–3000 cm^{-1} which may be assigned to the aromatic ν(C—H)[7,8]. The

TABLE-1
ANALYTICAL DETAILS OF THE VARIOUS SELENIUM(IV) DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

S.No.	Compound (molar ratio) (colour)	m.p. (°C)	Analysis % Found (Calcd.)			
			C	H	N	Se
1.	$Se(OPr^i)$(hmba-3) (1:1) (light brown)	275	50.35 (50.43)	5.72 (5.74)	4.18 (4.20)	23.65 (23.68)
2.	$Se(Hhmba\text{-}3)_2$ (1:2) (brown)	280	54.87 (54.92)	5.42 (5.44)	5.80 (5.82)	16.37 (16.41)
3.	$Se(OPr^i)(H_2hmba\text{-}3)_3$ (1:3) (dark brown)	285	57.60 (57.65)	6.56 (6.58)	5.58 (5.60)	10.30 (10.40)
4.	$Se(H_2hmba\text{-}3)_4$ (1:4) (brown)	270	57.63 (57.77)	6.15 (6.17)	6.10 (6.12)	8.37 (8.38)
5.	$[Se(OPr^i)]_2(Hhmba\text{-}3)_3$ (2:3) (brown)	>300	52.26 (52.28)	5.94 (5.96)	4.68 (4.69)	17.58 (17.62)
6.	$Se(OPr^i)$(hmba-6) (1:1) (brown)	245	50.35 (50.43)	5.72 (5.74)	4.18 (4.20)	23.66 (23.68)
7.	$Se(Hhmba\text{-}6)_2$ (1:2) (dark brown)	220	54.80 (54.92)	5.42 (5.44)	5.80 (5.82)	16.38 (16.41)
8.	$Se(OPr^i)(H_2hmba\text{-}6)_3$ (1:3) (dark brown)	230	57.60 (57.65)	6.57 (6.58)	5.58 (5.60)	10.37 (10.40)
9.	$Se(H_2hmba\text{-}6)_4$ (1:4) (cream)	235	57.70 (57.77)	6.15 (6.17)	6.10 (6.12)	8.37 (8.38)
10.	$[Se(OPr^i)]_2(Hhmba\text{-}6)_3$ (2:3) (cream)	240	52.15 (52.28)	5.95 (5.96)	4.68 (4.69)	17.60 (17.62)
11.	$Se(OPr^i)$(hmba-5) (1:1) (grey)	179	50.35 (50.43)	5.72 (5.74)	4.19 (4.20)	23.65 (23.68)
12.	$Se(Hhmba\text{-}5)_2$ (1:2) (brown)	178	54.85 (54.92)	5.42 (5.44)	5.80 (5.82)	16.38 (16.41)
13.	$Se(OPr^i)(H_2hmba\text{-}5)_3$ (1:3) (brown)	180	57.60 (57.65)	6.56 (6.58)	5.58 (5.60)	10.36 (10.40)
14.	$Se(H_2hmba\text{-}5)_4$ (1:4) (dark brown)	182	57.65 (57.77)	6.15 (6.17)	6.10 (6.12)	8.34 (8.38)
15.	$[Se(OPr^i)]_2(Hhmba\text{-}5)_3$ (2:3) (brown)	176	52.19 (52.28)	5.94 (5.96)	4.68 (4.69)	17.58 (17.62)

Abbreviations: $OPr^i = OC_3H_7$, H_3hmba-3 (or -6 or -5): $CH_3C_6H_3(OH)CH_2\overset{+}{N}H_2CH(CH_3)COO^-$

band corresponding to the phenolic (—OH) group, as observed in H_3hmba-3, is found to be absent here suggesting the bonding of the phenolate oxygen with selenium. The peaks due to ν(C—H) of the $—CH_2—$ and $—CH_3$ groups[7] appear at 2950 cm^{-1} and 2840 cm^{-1}. The band due to the $>\overset{+}{N}H_2$ group is observed to disappear here and no peak corresponding to the >NH group is noticed which suggests possible bonding of nitrogen to selenium. The absence of any characteristic band corresponding to the C=O group in the region 1750–1650 cm^{-1} rules out the possibility of a normal ester type of linkage between the carboxylate

TABLE-2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF THE VARIOUS SELENIUM(IV) DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

Compound	ν(—OH)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_3 and —CH_2— groups	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Se–N)	ν(Se–O)
Se(OPr^i)(hmba-3)	—	*3150–3000 (mb)	2950 (m) 2840 (m)	1600 (vsb)	1390 (sh)	210	1250 (s)	740 (m) 670 (w)	515 (m) 485 (m)
Se(Hhmba-3)$_2$	—	3250–3000 (vsb)	2900 (w)	1600 (sb)	1380 (m)	220	1250 (s)	740 (m) 680 (m)	520 (m) 480 (m)
Se(OPr^i)(H$_2$hmba-3)$_3$	3500–3300 (vsb)	3200–3000 (mb)	2940 (m)	1600 (sb)	1390 (m)	210	1255 (vs)	740 (m) 690 (w)	530 (m) 470 (m)
Se(Hhmba-3)$_4$	3500–3300 (vsb)	3200–3000 (mb)	2920 (w)	1610 (sb)	1390 (m)	220	1260 (s)	735 (m) 680 (s)	510 (m) 490 (m)
[Se(OPr^i)]$_2$(Hhmba-3)$_3$	—	3250–3000 (mb)	2940 (m) 2860 (w)	1605 (sb)	1390 (sb)	215	1260 (s)	670 (s)	520 (w) 485 (w)
Se(OPr^i)(hmba-6)	—	*3100–3000 (mb)	2920 (w)	1630 (sb)	1385 (m)	245	1270 (s)	740 (vw) 680 (m)	520 (w) 480 (w)
Se(Hhmba-6)$_2$	—	3250–3000 (b)	2960 (w) 2860 (w)	1630 (sb)	1380 (mb)	250	1260 (s)	680 (s)	520 (w) 480 (m)
Se(OPr^i)(H$_2$hmba-3)$_3$	3500–3300 (mb)	3150–3000 (b)	2940 (w)	1630 (vsb)	1380 (mb)	250	1260 (s)	740 (m) 680 (s)	520 (w) 480 (m)

TABLE 2 (Contd.)

Compound	ν(—OH)	ν(N—H) and aromatic ν(C—H)	ν(C—H) of —CH_3 and —CH_2— groups	ν_{asym}(COO)	ν_{sym}(COO)	Δν(COO)	ν(C—N)	ν(Se–N)	ν(Se–O)
$Se(H_2hmba\text{-}6)_4$	3550–3300 (mb)	3230–3000 (mb)	2980 (m) 2860 (w)	1630 (sb)	1385 (m)	245	1270 (s)	680 (s)	510 (m) 490 (m)
$[Se(OPr^i)]_2(Hhmba\text{-}6)_3$	—	3200–3000 (mb)	2920 (w)	1630 (sb)	1380 (mb)	250	1270 (m)	680 (vw)	520 (w) 485 (m)
$Se(OPr^i)(hmba\text{-}5)$	—	*3200–3000 (mb)	2915 (w)	1630 (sb)	1390 (s)	240	1260 (m)	690 (w)	510 (vw) 480 (m)
$Se(Hhmba\text{-}5)_2$	3600–3300 (b)	3200–3000 (mb)	2920 (m)	1625 (sb)	1380 (m)	245	1270 (m)	685 (s)	530 (w) 480 (m)
$Se(OPr^i)(H_2hmba\text{-}5)_3$	3600–3300 (b)	3200–3000 (mb)	2920 (w) 2840 (w)	1630 (sb)	1380 (m)	250	1260 (s)	690 (w)	530 (w) 470 (m)
$Se(H_2hmba\text{-}5)_4$	3500–3300 (vsb)	3200–3000 (mb)	2910 (m)	1625 (sb)	1370 (m)	255	1270 (vs)	680 (m)	520 (vw)
$[Se(OPr^i)]_2(Hhmba\text{-}3)_3$	—	3250–3000 (mb)	2920 (w)	1625 (sb)	1380 (s)	245	1270 (sb)	730 (vw) 690 (m)	520 (w) 485 (w)

Abbereviations: s = strong, m = medium, w = weak, vsb = very strong broad, sb = strong broad, mb = medium broad, vw = very weak, sh = shoulder.
*due to aromatic ν(C—H) alone.

TABLE-3

PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ value) OF SEVERAL SELENIUM(IV) DERIVATIVES OF N-(*o*-HYDROXY SUBSTITUTED BENZYL) ALANINES

S. No.	Compound	Aromatic ring	Phenolic (—OH)	>CH—	>NH—	CH_3 attached with the benzene ring	—CH_2—	—CH_3 of the alanine part	Gem dimethyl
1.	$Se(OPr^i)$(hmba-3)	6.45–7.25 (m)	—	3.30–3.90 (q)	—	2.30 (s)	2.05 (d)	1.10 (d)	1.05 (d)
2.	$Se(Hhmba\text{-}5)_2$	6.40–7.30 (t)	—	3.40–3.95 (bm)	3.05 (s)	2.25 (s)	2.05 (d)	1.15 (d)	
3.	$Se(OPr^i)(H_2hmba\text{-}3)_3$	6.40–7.30 (m)	5.50 (s)	3.50–3.85 (m)	3.05 (s)	2.25 (s)	2.05 (d)	1.15 (d)	0.90 (d)
4.	$Se(H_2hmba\text{-}3)_4$	6.50–7.00 (m)	5.65 (s)	3.40–3.90 (m)	3.00 (s)	2.20 (s)	2.05 (d)	1.15 (d)	—
5.	$[Se(OPr^i)]_2(Hhmba\text{-}6)_3$	6.55–7.25 (t)	--	3.40–3.80 (m)	3.10 (s)	2.20 (s)	2.05 (d)	1.15 (d)	1.00 (d)

Abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bm = broad multiplet.

oxygen and selenium[7]. A very strong broad band occurring at 1600 cm^{-1} may be attributed to the overlapping of ν_{asym}(COO) and aromatic ν(C=C)[8, 9]. The weak and strong bands respectively at 1500 cm^{-1} and 1460 cm^{-1} may be assigned to the overlapping of ν_{sym}(COO), C—H bending and the aromatic skeletal vibrations[8, 11]. Further, instead of a peak at 1405 cm^{-1}, as noted in H_3hmba-3, here a medium band around 1390 cm^{-1} with a shoulder may be assigned to the overlapping of ν_{sym}(COO) and C—H bending due to the *gem* dimethyl structure of the isopropoxy group[8, 9]. A shift of 15 cm^{-1} in ν_{sym}(COO), as compared to H_3hmba-3, shows the bonding of carboxylate oxygen with selenium. The separation value, $\Delta\nu$(COO) of 210 cm^{-1}, as observed here, suggests the absence of a bridged or coordinated carboxylate group[12–14]. The strong peaks at 1250 cm^{-1} and 1220 cm^{-1} correspond to ν(C—N) and ν(C—O) respectively[7]. Thus, a shift of 20 cm^{-1} in ν(C—N), as compared to H_3hmba-3, shows possible bonding of nitrogen to selenium. The medium bands at 1150 cm^{-1}, 1105 cm^{-1}, 1080 cm^{-1} and 1020 cm^{-1} may be ascribed to the aromatic C—H in-plane bending[8, 15], while those at 950 cm^{-1}, 870 cm^{-1} and 800 cm^{-1} correspond to the aromatic C—H out-of-plane bending of a trisubstituted benzene ring[8]. The medium and weak absorptions at 740 cm^{-1} and 670 cm^{-1} occur due to ν(Se—N) while the medium peaks at 515 cm^{-1} and 485 cm^{-1} correspond to ν(Se—O)[16].

It is thus evident that the selenium atom in Se(OPr^i)(hmba-3) [Structure (II)] shows tetravalency as a result of bonding with one of the oxygens from the carboxylate group, the oxygen from the phenolate group and the nitrogen obtained by the deprotonation of $>\overset{+}{N}H_2$ group along with an isopropoxy group.

The PMR spectrum of Se(OPr^i)(hmba-3) displays a multiplet between δ6.45–7.25 which may be attributed to the aromatic ring protons[9, 17]. The absence of a singlet at δ6.75 due to the proton of the phenolic group, as noted in H_3hmba-3, indicates the deprotonation of the phenolic group as a result of binding of the phenolate oxygen with selenium. A hump in the region δ3.20–3.40 due to the protons of the $>\overset{+}{N}H_2$ group, as observed in H_3hmba-3, is found to be absent here suggesting the bonding of nitrogen to selenium. A quartet corresponding to the >CH— group proton of the alanine part of H_3hmba-3 occurs here between δ3.30–3.90, while the signals due to the protons of the —CH_3 and —CH_2— groups attached with the benzene ring of H_3hmba-3 appear as a singlet at δ2.30 and a doublet at δ2.05, respectively. A doublet at δ1.10 corresponds to the protons of the —CH_3 group of the alanine part of H_3hmba-3, while another at δ1.05 may be assigned due to the *gem* dimethyl protons of the isopropoxy group[14, 17, 18]. Thus the inferences drawn here are in conformity to those derived from IR measurements earlier.

The IR and PMR spectral data were similarly interpreted for the other derivatives and the main findings in the context of their structures are as under:

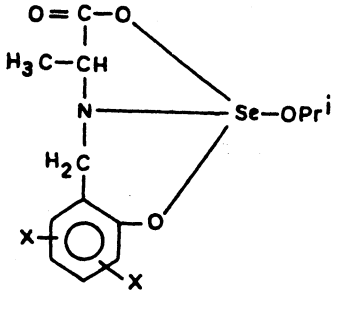
The selenium atom in $Se(OPr^i)$(hmba-6) and $Se(OPr^i)$(hmba-5) (structure II) exhibits tetravalency in each case by way of similar modes of bonding, as those observed in case of $Se(OPr^i)$(hmba-3).

The derivatives, Se(Hhmba-3)$_2$, Se(Hhmba-6)$_2$ and Se(Hhmba-5)$_2$ (structure III) contain a hexa-coordinated selenium atom in each case as a result of bonding with one of the oxygens from each of the two carboxylate groups, the oxygen from each of the two phenolate groups and the nitrogen from each of the two imino groups available from two modes of I.

Selenium atom in $Se(OPr^i)(H_2hmba\text{-}3)_3$, $Se(OPr^i)(H_2hmba\text{-}6)_3$ and $Se(OPr^i)(H_2hmba\text{-}5)_3$ (IV) displays penta-coordination in each case by way of bonding with one of the oxygens from each of the three carboxylate groups and the nitrogen from each of the three imino groups available from three moles of I, along with an isopropoxy group.

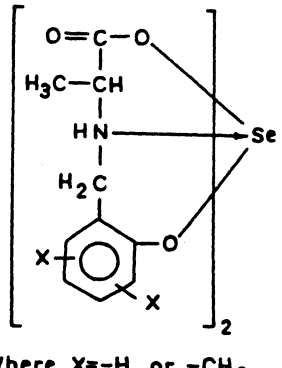
The derivatives, $Se(H_2hmba\text{-}3)_4$, $Se(H_2hmba\text{-}6)_4$ and $Se(H_2hmba\text{-}5)_4$ (structure V) contain an octa-coordinated selenium atom in each case as a result of bonding with one of the oxygens from each of the four carboxylate groups and the nitrogen from each of the four imino groups available from four moles of I.

It is rather difficult to assign any definite structure for $[Se(OPr^i)]_2$(Hhmba-3)$_3$, $[Se(OPr^i)]_2$(Hhmba-6)$_3$ and $[Se(OPr^i)]_2$(Hhmba-5)$_3$ on the basis of the available data. Adaptation of more sophisticated techniques would be required to arrive at an umambiguous conclusion, which is not possible under the existing facilities of these laboratories.



Where X=-H or $-CH_3$

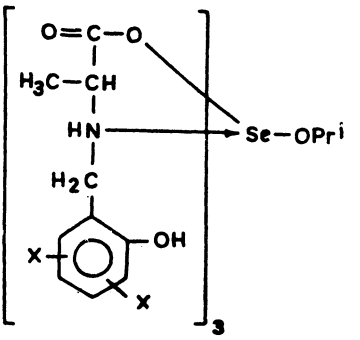
(II)



Where X=-H or $-CH_3$

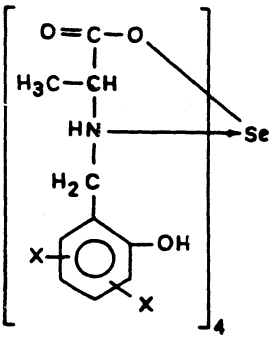
(III)

[Contd.]



Where X=-H or-CH_3

(IV)



Where X=-H or -CH_3

(V)

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(*Received*: 3 January 1994; *Accepted*: 28 May 1994) AJC-822